Development and Application of Fluorescent Diagnostics to Fundamental Droplet and Spray Problems

Final Report

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I. STATEMENT OF THE PROBLEM STUDIED

The purpose of the work described in this final report is to develop and apply fluorescent diagnostics for the understanding of evaporation and heat transfer processes in hydrocarbon fuel droplets in both isolated and fuel spray environments. In the course of the investigations, experimental and computational techniques have been developed (a) for correcting images of an equatorial "slice of sub-millimeter diameter droplets, (b) for exciplex fluorescence thermometry (and a new modification, exciplex shift thermometry) of evaporating droplets, (c) for generation of droplets with defined initial internal circulation patterns, which has led to demonstration that aerodynamic shear can induce internal circulation in sub-millimeter droplets, and (d) for two dimensional imaging of radiative lifetimes (equivalence ratio imaging and vapor temperature imaging).

It is hoped that the demonstration of the availability and utility of these new techniques will lead to their use in clarifying the basic physical processes involved in the heating and vaporization of sub-millimeter droplets.

L. A. Melton at the University of Texas at Dallas (UTD) has served as the principle investigator on this grant. Michael Winter at United Technologies Research Center (UTRC) is the principal scientist on the subcontract to UTRC. In so far as possible, individual results described in the text are labelled by the source of the work.

II. SUMMARY OF MOST IMPORTANT RESULTS

A. Thermometry

1. Diagnostic Development

a. Identification of Potential Systematic Errors in Exciplex Fluorescence Thermometry of Droplets (UTD)

Under a prior ARO program, Thomas Hanlon at UT-Dallas had used exciplex fluorescence thermometry (EFT) to infer hexadecane droplet temperatures as a function of fall distance in quiescent heated nitrogen; his inferred temperatures showed a striking (and unrealistic) jump of about 100 ^{o}C once the droplet reached a temperature of approximately 80 ^{o}C.[2] Under this program, Dr. Zhang Jingyi has shown that a proper explanation of Hanlon's results requires inclusion of (1) the optics of the droplet, (2) the transient temperature field within the droplet, and (3) the nonlinear characteristics of the exciplex fluorescence thermometry calibration curve. On the basis of Zhang's work, it has been shown that experiments such as those

carried out by Hanlon can be (1) designed so that the optical weighing of fluorescence from within the droplet matches the geometrical weighting, i.e., unbiased transient volume-averaged temperatures are obtained, and (2) interpreted so that the anomalous temperature "step" yields directly the vapor-to-liquid heat transfer coefficient.[3] This analysis shows further how to estimate and sometimes eliminate several sources of systematic error in the EFT determination of droplet temperatures. The anomalous "jump" was shown to be a result of the concave nature of the EFT calibration curve, and thus Zhang's finding that, if the calibration curve for exciplex fluorescence thermometry shows a linear variation of the ratio of the exciplex emission intensity to the monomer emission intensity as a function of temperature, then this anomalous "jump" becomes negligible.

b. Exciplex Shift Thermometry (UTD)

In the course of experiments designed to measure the temperature of evaporating decane droplets, it was found that the PYPYP exciplex thermometry system, which had worked well for Hanlon's experiments on falling hexadecane droplets, did not give reliable results when used with decane. The decane being less viscous, allowed more of the exciplex to form in the low temperature, kinetic control regime below 80 ^{o}C. As a result, the monomer intensity was too small, compared to the exciplex intensity, to measure reliably.

At this point, the temperature dependent shift of the exciplex band to lower wavelengths with increasing temperature was exploited. In addition to providing an alternate thermometry system which would be usable in low viscosity solvents, it was hoped that, if the exciplex band resulted from the transitions of a single species, then quenching by oxygen would lower the intensity of the exciplex band but would not affect its shape, i.e., the exciplex shift thermometry systems (EST) would be insensitive to oxygen quenching so long as adequate intensity was obtained for the fluorescence measurements.

The "exciplex shift thermometers" are less sensitive than the previous "exciplex/monomer ratio thermometers", i.e., yield temperatures +/- 10 ^{o}C rather than +/- 2-3 ^{o}C, but are also much less perturbed by oxygen and can be used in air up to a pressure of 1 atmosphere. However, they are not completely insensitive to quenching by oxygen, and their use is limited to air pressures less than or equal to approximately one atmosphere. The calibration curves appear to be identical in decane and hexadecane, which suggests that this exciplex shift thermometer can be used in to study multicomponent evaporation processes.

The basic phenomena which cause the shift of the exciplex emission to higher energies as the temperature increase are not yet well understood.

c. Vapor Temperature Imaging (UTD)

In the course of experiments using fluorescence lifetime imaging (FLI) for equivalence ratio imaging (ERI),[4] [see also paragraph II.B.3] it became apparent that the fluorescence lifetime of the fluorescent dopant, fluoranthene, was temperature dependent, a substantial complication for the ERI method. It was decided to exploit this discovery, and thus naphthalene, which has an even stronger dependence of its fluorescence lifetime on temperature, was chosen as a fluorescent dopant for which the temperature dependence of its lifetime could be used to image the temperature of a vapor field. However, because oxygen also shortens the lifetime of naphthalene, in order to have an interpretable thermometer, it is necessary to exclude oxygen from the gas flow under study.

The lifetime was measured as a function of temperature (180 nsec at 20 ^{o}C, 35 nsec at 450 ^{o}C). Two streams of nitrogen were passed over naphthalene in order to "seed" them. One stream was heated, and coflow experiments (either hot center/cold outside or cold center/hot outside) were carried out. As a result temperature field were determined for laminar and turbulent mixing conditions.[7]

2. Applications

a. Evaporating Decane Droplets (UTD)

The droplet fall tube which Hanlon used in experiments has been modified. A larger heating element allows the maximum temperature of the ambient nitrogen to reach 650 ^{o}C, in stead of the 550 ^{o}C Hanlon obtained. At this nitrogen temperature 80% of the decane droplet mass can be evaporated in the 10 cm fall distance within the fall tube. Temperature measurements ("volume averaged temperatures") of falling evaporating decane droplets were attempted. The temperature calibrations proceeded routinely, but instabilities in the lateral position of the droplet caused problems in obtaining reproducible positioning of the exciplex spectrum on the OMA (optical multichannel analyzer). Ultimately, a solution to these experimental problems was devised, but by that time, it had become clear that droplet slicing imaging (DSI) combined with exciplex fluorescence thermometry (EFT) would give much more important thermometry information, and these measurements were not pursued.

b. Spray onto Heated Plate (UTD)

This work was not supported by funds from this ARO program, but it is mentioned here as an example of the transfer of technology developed under this and prior ARO programs to the civilian sector, in particular to address problems which Ford Motor Company has found in their engine development programs.

The experiment consisted of a fuel injector, supplied by Ford, which delivered a few millisecond pulse of fuel onto a heated steel plate. The laser was fired 0 - 200 milliseconds after the spray, and exciplex shift thermometry was used to image the two dimensional temperature distribution of the residual liquid. The temperature images obtained with decane and hexadecane were supplied to Ford, and a three year scientific program has resulted.

B. Diagnostics for Combustion Systems

1. Quenching by Nitrous Oxide (UTD)

Paul Ronney, then at Princeton University, suggested that, with O_2 being such an effective and ubiquitous quencher, it might be possible to study combustion using N_2O flames. The photophysical literature contains very little in the way of studies of the quenching of fluorescence by N_2O, and it seemed, on the basis of arguments about the properties of efficient quenchers that N_2O might be a very inefficient quencher. The quenching of the fluorescence of naphthalene and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), the two components of the best exciplex-based vapor/liquid visualization system, by nitrous oxide was studied. The quenching is, indeed, inefficient. However the quenching of TMPD by N_2O, although twenty times less efficient than the quenching by O_2, is still too efficient to allow quantitative use of napthalene/TMPD exciplex-based vapor/liquid visualization systems under N_2O supported combustion conditions.

2. Caged Molecules, Resistant to Oxygen Quenching (UTD)

On October 1, 1992, Melton visited the Wright Aeronautical Laboratories at Wright-Patterson AFB (W. M. Roquemore) and gave a seminar describing the fluorescent diagnostic work supported by this grant. As a result of this visit, he learned of work carried out at Michigan State University in which Daniel Nocera has synthesized classes of organometallic molecules whose fluorescence is virtually unquenched by oxygen. The molecules have not been studied under this program, but their existence suggests that it may be possible to develop thermometry and/or visualization systems which are usable under combustion conditions.

3. Equivalence Ratio Imaging (UTD)

Fast gated imaging equipment, which was purchased under ARO proposal 28890-EG-EQ, has been used to produce two dimensional PLIF images of the fuel/oxygen equivalence ratio in methane jets and methane diffusion flames.[4] The experiments extend the liquid phase "proof of concept" experiments described in 1991 to realistic gas phase systems. As before, the fluorescent dopant is fluoranthene, which is very inefficiently quenched by molecular oxygen. Unfortunately, the fluorescence lifetime of fluoranthene decreases significantly with increasing temperature, and thus the images are rigorously interpretable only in isothermal systems.

C. Droplet Slicing Imaging

1. Tests of Droplet Generators (UTRC)

Michael Winter has investigated methods for preparing droplets with known prior internal circulation patterns so that droplet slicing imaging (DSI) techniques could be used to determine unambiguously whether aerodynamically-induced internal circulation is significant in sum-millimeter diameter droplets. Droplets frozen in liquid nitrogen have been suspended in a levitator and allowed to thaw; the resulting droplet should have no internal circulation. Unfortunately, droplets of volatile liquids are difficult to suspend stably. Droplets can be formed by suspending liquid on the end of thin fiber and then yanking the suspension fiber out of the pendant droplet quickly. This should result in internal circulation flows counter to those which would be induced by aerodynamic forces. Unfortunately, the subsequent droplet trajectory is not reproducible, and DSI measurements cannot be made. Aerodynamic droplet generators, in which the flow of gas through a nozzle is used to strip droplets off a hypodermic needle centered in the nozzle, have proven to be simple, effective sources for droplet studies. The initial flow pattern is counter to that which will be induced by later fall of the droplet. The droplet trajectories are reproducible, even under transition turbulence conditions. In applications at UTRC, outside this program, the aerodynamic droplet generators have been used to produce "supercritical" droplets of oxygen.

2. Improvements in Droplet Slicing Imaging Techniques

a. Resolution (UTRC)

Using a Questar QM100 long working distance microscope with UV quartz optics, acquired with UTRC funds,

Michael Winter has obtained "droplet slicing" images of naphthalene doped droplets falling into air at high resolution, approximately 1.2 microns/pixel. With this resolution, it is possible to see multiple streamlines and/or vortices within the droplet.

b. Aerodynamic Shear Demonstrated (UTRC)

Michael Winter obtained "droplet slicing" images of falling naphthalene doped droplets and showed for the first time that aerodynamic drag does induce internal circulation in submillimeter diameter droplets. By use of an aerodynamic droplet generator with air as the surrounding gas, it was shown that the internal circulation is in the expected direction when the ambient air is moving faster than the droplet and reverses direction when the droplet is moving faster than the (finally) quiescent air.

c. Layered droplets (UTRC)

Droplet slicing imaging experiments have been carried out with naphthalene doped droplets combined with acetone seeded gas in the flow of an aerodynamic droplet generator. The hope, which was realized, was to image the internal circulation patterns in the droplet [by streamlines by oxygen quenching (SOQ)] and the droplet-induced turbulence in the gas phase, simultaneously by acetone fluorescence PLIF. However, serendipitously, acetone condensed on the surface of the (cold) and produced a "layered droplet". The naphthalene was not needed; the internal circulation patterns in the "layered droplet" could be followed by the acetone fluorescence from the droplet. In addition, it was found that acetone condenses continuously on the outer surface of the droplet, and the acetone is subsequently carried into the interior of the droplet by convection. In comparison with the SOQ imaging techniques, the "layered droplet" technique yields stronger fluorescence signals (even though the fluorescence quantum yield of acetone is much lower than that of naphthalene, it is present in higher local concentrations), enhanced contrast and dynamic range (acetone fluorescence is viewed against a dark background while oxygen-quenched naphthalene fluorescence is viewed against a light background), and more sharply defined streamlines (acetone diffuses less rapidly in the liquid phase than oxygen). In addition, the "layered droplet" approach can be employed to study droplet-environment interactions in combustion systems, since oxygen is not the indicating species.

d. Droplets in flames (UTRC)

If the gas flow in an aerodynamic droplet generator is changed from nitrogen to a methane/nitrogen mixture, the exiting gas flow can be ignited to produce a

turbulent methane diffusion flame. The droplet generator still works well, although it is now more convenient to orient the generator so that the gas flow is up rather than down. The resulting droplets pass from the relatively cold interior of the diffusion flame and through the flame front. "Layered droplet"/DSI techniques can be used to study the droplet flow patterns. If the interior of the diffusion flame is truly oxygen-free, as can be determined by measurement of the fluorescence lifetime of naphthalene vapor, then conventional exciplex fluorescence thermometry systems can be used to follow the droplet temperature patterns. This discovery was made late in the program and. although DSI in such a flame has been demonstrated, there was not time to pursue other results.

5. Algorithms and Computer Programs to Correct for Effect of Droplet Refraction (UTD)

Algorithms and computer programs have been developed to remove the effects of refraction by the front hemisphere of the droplet and to recover the corrected streamline image.[5] The reverse mapping, to obtain the corrected image, is quite unstable numerically and it was necessary to resort least squares fitting of radial expansions in a combined polynomial/Fourier basis set in order to obtain reliable numerical results, particularly for intensities a radial coordinates greater than 70% of the droplet radius. Even so, it appears that, for images taken at 90^{o} with respect to the incident laser sheet, the image can be recovered out to approximately 80% of the droplet radius; beyond that point, recovery is so unstable that it is infeasible. However, modified algorithms show that for images taken at $50-70^{o}$ with respect to the incident laser sheet, the image can be recovered all the way to the near edge of the droplet; thus by sacrificing a portion of the far edge portion of the image it is possible to obtain quantitative information on the near surface fluorescent intensity field.

Image files were initially transferred electronically from UTRC to UTD, processed, and returned electronically to UTRC. Later, the computer programs were successfully exported to UTRC, along with a "User's Manual", and subsequently UTRC has carried out its own image corrections. The computer programs and "User's Manual" have been distributed, without charge, to any user who requests them.

6. Droplet Slicing Imaging/Exciplex Shift Thermometry Experiments (UTD)

Initial droplet slicing imaging experiments were carried out at UTD, with the intent of learning DSI techniques and applying them to measurement of the temperature field inside a rapidly heating droplet. There was not time in this program to carry out thermometry experiments.

III. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

(1) T. Q. Ni and L. A. Melton, "Fluorescence Lifetime Imaging: An Approach for Fuel Equivalence Ratio Imaging", Appl. Spectroscopy, 45, 938 (1991). *

(2) T. R. Hanlon and L. A. Melton, "Exciplex Fluorescence Thermometry of Falling Hexadecane Droplets", Journal of Heat Transfer, **114**, 450 (1992).*

* mentioned in ARO Final Report, DAAL03-87-K-0120, July 1991.

(3). J. Zhang and L.A. Melton, "Potential Systematic Errors in Droplet Temperatures Obtained by Fluorescence Methods", J. Heat Transfer, **115**, 325 (1993).

(4). T.Q. Ni and L. A. Melton, "Fuel Equivalence Ratio Imaging for Methane Jets", Applied Spectroscopy, **47**, 773 (1993).

(5) Jingyi Zhang and L.A. Melton, "Numerical Simulations And Restorations of Laser Droplet-Slicing Images", Applied Optics, **33**, 192 (1994).

(6). L.A. Melton, "Planar Liquid and Gas Visualization", Berichte der Bunsen-Gesellschaft fur Physikalische Chemie, **97**, 1560 (1993).

(7). T.Q. Ni and L.A. Melton, "2-D Gas Phase Temperature Measurements Using Fluorescence Lifetime Imaging", submitted to XXVth Symposium (Int.) on Combustion; not accepted because of limited relevance; to be submitted to Applied Spectroscopy.

(8). Michael Winter, "Droplet Slicing Measurements in Single and Bicomponent Layered Droplets", submitted to XXVth Symposium (Int.) on Combustion; not accepted because of limited relevance.

(9) L.A. Melton, "Planar Liquid and Gas Visualization", presented at Eighth International Focurm on

Pracess Analytical Chemistry, Montgomery, TX, January 24-26, 1994; accepted for publication AT-Process.

(10) Michael Winter, "Droplet Slicing Measurements of Internal Circulation", AIAA 93-0900, 31st Aerospace Sciences Meeting and Exhibit, January 11-14, 1993, Reno, NV.

IV. PARTICIPATING SCIENTIFIC PERSONNEL

1. Lynn A. Melton, principal investigator
   Professor of Chemistry
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2. Michael Winter
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3. Susan Eshelman, graduate student, M.S. degree awarded May 1992

4. Oscar Arce, graduate student, M.S. degree awarded May 1993

5. Yadong Zhao, graduate student, M.S.. degree expected August 1996

6. Jingyi Zhang, postdoctoral scientist, currently with Professor Joseph Katz, Johns Hopkins University

7. Tuqiang Ni, postdoctoral scientist, currently with Professor Robert Santoro, Pennsylvania State University

8. Qingzheng Lu, postdoctoral scientist

9. John Blair, technician

10. L.D. Brooks, technician

V. REPORT OF INVENTIONS

No inventions developed during this period.

However, a patent disclosure ("Method for Imaging of Gas Phase Temperature Field Using Fluorescence Lifetimes") was prepared under the University of Texas Intellectual Property Policy. The University of Texas at Dallas Intellectual Property Committee recommended to the University of Texas System that they should not pursue a patent on the disclosed method, and the University of Texas System concurred. Consequently DOD form 882 was not filed.

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13. ABSTRACT *(Maximum 200 words)*

This final report describes work carried out under ARO grant DAAL03-91-G-0033 for the development and application of fluorescent diagnostics to fundamental droplet problems. Particular emphasis has been placed on attempts to understand the heating, evaporation, and internal circulation processes of sub-millimeter droplets. At the University of Texas at Dallas, a new type of exciplex fluorescence thermometer, based on the temperature dependent shift of the exciplex band, has been developed and applied to thermometry of evaporating droplets and surface liquids. Algorithms and programs have been developed and disseminated for the correction of "droplet slicing images" (DSI) for the effects of refraction by the front hemisphere of the droplet. At United Technologies Research Center, DSI techniques have been used to demonstrate unequivocally that aerodynamic shear can induce internal circulation in sub-millimeter droplets and to show that droplets rotate and interact with the surrounding gas phase flow field.

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